



Thermodynamics (Entropy and Gibbs Free Energy)

AP Chemistry



Remember Thermochemistry?

All the way back in early 2nd quarter?

The study of Thermochemistry is really looking at one aspect of Thermodynamics.

Specifically, we looked at heat transfer - or the study of the idea of enthalpy. (ΔH) You can't say how much heat an object has - but you can measure the transfer of it.



Enthalpy is just one part of the picture

So, I'm going to start with the ending equation.

We'll talk about each part. We'll focus on one component (entropy, also the name of the old U2 fan club), then Gibbs free energy. Then, we'll put it all in a blender and see how it all comes out together.



A final word on enthalpy

Enthalpy is the heat transfer component - it's our endothermic/exothermic marker. If a reaction or process releases energy to the surroundings, it's EXOthermic. If it takes energy in from the surroundings, it's ENDOthermic.

It can't be the only factor in determining if a reaction happens. Logically, both "cold" and "warm" things happen on their own. There has to be another factor(s). So, let's talk about it.



The final equation

I'm omitting the delta symbols because it will take forever to type otherwise; please excuse my laziness.

The final equation is: $G = H - (T \times S)$ Delta's for change in front of G, H, & S

G is change in Gibbs Free Energy; H is change in enthalpy

S is change in entropy.



What are the other factors?

Gibbs Free Energy → This is the overall factor. We use this to predict if a process is THERMODYNAMICALLY FAVORABLE (old-school term is spontaneous; it's a bit misleading; don't use it). If the reaction happens (you witness it), it's thermodynamically favorable (or you can calculate it). If it doesn't (or the the calculation doesn't support it), it won't (unless you drive it by coupling it with one that is)



What are the other factors?

Gibbs Free Energy → If this value is negative, the process is thermodynamically favorable; if it's positive, it isn't favorable.

We'll bring up more about this in a bit, but now let's talk about entropy.



What are the other factors?

Entropy → You will see this discussed as dispersion (or referred to a disorder, which is a bit incorrect, but gets the point across).

I have a deck of cards; let's run a few scenarios through.

Does anyone want to play 52 pick-up with me?



What are the other factors?

Let's take some bets. What are the chance that:

We launch the cards in the air, and they land in a pile?

That they land in a stack? In a stack in the exact same order?

That they land scattered? How scattered are they?



What are the other factors?

Tell me about the process of putting the deck of cards back together again?

About putting them back together - all black and all red together?

Together in suits - spades, hearts, clubs, and diamonds?

In suits, in numerical order, going from 2 to ace?



This is all entropy

Entropy is a mathematical situation - things generally proceed to the greatest number of possibilities - which generally means disorder (but always means dispersion, which occasionally does some odd seeming things).

Unless we spend energy to create order (or less dispersion), things will proceed to dispersion.



Sidebar

This is why scientist talk about the universe eventually going to “useless” forms of energy. The tendency is for energy to go to dispersion/disorder. We have to work extra to create order for us; in doing so, we create more disorder. Eventually, that will catch up to us, and from a dispersion standpoint, we’re collectively hosed.



Before going forward

Laws of thermodynamics:

1st - Energy not created nor destroyed; it just changes forms (conservation of energy). 2nd - Universe constantly increasing dispersal of matter and energy. 3rd - Entropy of a perfect crystal at 0K is zero (can't happen).

(Can't win, can only hope to break even, can't get out of the game)



Entropy

Now you have a conceptual idea of what entropy is; let's define a direction.

If more energy is dispersed (which is more likely), this is more favorable - this value is POSITIVE. If less energy is dispersed (more order is created in a manner of speaking), this is considered to be the negative direction.

Let's follow a few rules, and if it seems like there is something being broken, something has to be going on beneath the surface.



Entropy

Entropy increases as matter/energy is dispersed in a system (no, duh)

Entropy increases as you go from solid to liquid to gas. (Think about molecular motion and spacing)

Pure solids and liquids - when dissolved - almost always have their entropy increased (again, think about what's going about contact and spacing)



Entropy

When gas escapes a liquid, entropy increases (no, duh)

Entropy increases as the solid structure is more complicated. (think about the arrangement)

If your reaction produces more moles of something, entropy generally increases (you are breaking things into smaller bits; that's harder to put back together)



G, H, and S, it doesn't matter

For a process, it's always products - reactants

That's easy to remember. At least it's consistent

G for the process = G products - G reactants

H process = H products - H reactants

S process = S products - S reactants



So how do we use the overall equation?

Now you can see how to predict if something is thermodynamically favorable.

$G = H - (T \times S)$ Break it down. If G is negative, it's TF. So far, so good.
Both EXOthermic and ENDOthermic things happen. So the $(T \times S)$ factor must play a role in things.



How do we use the overall equation?

Remember this: Enthalpy is measured in kJ (kilojoules)

Entropy is measured in J (joules). So even though entropy counts (and it's multiplied by the temp in Kelvin), enthalpy has a head start. It counts more, and entropy has ground to make up.

Let's set up a table.



Let's put the combinations together

Enthalpy

+

-

Entropy +

++

-+

-

+-

--


$$G = H - (T \times S)$$

Combo #1 → H is negative; S is positive. G will always be negative. Look at the equation. These reactions are always thermodynamically favored (EXOthermic with greater energy dispersion)

Combo #2 → H is negative; S is negative. It depends. The (T x S) factor becomes positive. As long as it's small, H wins. So, at low temperatures, these still happen. So, EXOthermic with less dispersion happens at low temps.


$$G = H - (T \times S)$$

Combo #3 → **H is positive; S is positive.** It depends again. You need a negative G. Your H factor is positive. Now you need (T x S) to be big in order to be negative enough to overcome H. So, **ENDO**thermic reactions that create dispersion happen at **HIGH** temperatures.

Combo #4 → **H is positive; S is negative.** G is **ALWAYS** positive. These are never thermodynamically favored. These won't happen unless you couple them with a process that is TF.



Entropy and phase changes

Slow down and think. As you increase temp, the substance ABSORBS energy. So heating a substance is ENDOthermic. But the state goes from less dispersed to more. Solid to liquid and liquid to gas INCREASE entropy.

Removing heat from a substance is EXOthermic, but entropy decreases.

It's odd to think about it, but going from gas to liquid and liquid to solid is less dispersed, but exothermic.



Don't worry about page 5

We explained this by looking at the conditions under which a reaction is thermodynamically favorable. If a reaction is endothermic, large dispersion compensates at HI temps.

If a reaction is exothermic, it either a) always happens as dispersion increases or b) happens when dispersion decreases at low temps.



Other implications of Gibbs Free Energy

-At equilibrium, neither process is thermodynamically favored; therefore, Gibbs Free Energy is ZERO at equilibrium. (essentially, you are just in a vicious cycle until conditions change)

-You can relate G to the EQ constant ($G = \text{negative } R \Delta T \ln K$!) An oldie but a goodie: $G = -RT \ln K \rightarrow R$ is the energy R ($8.31 \text{ J}/(\text{mol} \times \text{K})$), T is temp in Kelvin, and K is your equilibrium constant. (you can even convert for pressure, I'll leave that conversion to page 7 of your packet; we did that in our EQ unit)



Other implications of Gibbs Free Energy

-In our last unit, we can use G with our oxidation/reduction potentials (essentially, we can find G from our electrochemical cells). I'll show the equation here, but we won't use for a few days; just know that we have a lot ways of figuring out if our proposed conditions are TF or not!

$G = -nFE$ (n is # moles of electrons transferred, F is a constant - you will be given it; E is the standard cell potential - you'll calculate that or be given that)



Thermodynamics

This was a short unit. When combined with thermochemistry, you can see the real predictive ability of these concepts.

G , S , and H are state functions. They don't have intrinsic values, we measure their changes - but that's enough. By tracking these things, we can predict the conditions when things are TF to happen.



Thermodynamics

We now have a mathematical relationship between heat transfer (enthalpy) and energy dispersion (entropy). They are separate but somewhat related concepts.

The 3 laws of thermodynamics (while briefly stated) really explain/reflect this relationship.



Our last few units

Thermodynamics tell us IF a reaction happens.

Kinetics tells us how quickly it happens.

Equilibrium tells us where the endpoints is and where the balance lies.

You can't really talk chemistry until you can see these relationships.



Like always

We have to work a few problem sets, and then we move on to our last unit.

And then we review like made.

Buckle up, buttercup! One last big idea!



Extra Resources - Reading

Entropy:

<https://courses.lumenlearning.com/boundless-chemistry/chapter/entropy/>

Gibbs Free Energy:

<https://courses.lumenlearning.com/boundless-chemistry/chapter/gibbs-free-energy/>



Extra Resources - Video

Entropy:

<https://www.youtube.com/watch?v=MALZTPsHSoo&index=57&list=PLIIVwaZQkS2op2kDuFifhStNsS49LAXkZ>

Spontaneous Processes (thermodynamically favorable!):

<https://www.youtube.com/watch?v=hNSD0YDsPsE&index=58&list=PLIIVwaZQkS2op2kDuFifhStNsS49LAXkZ>



Extra Resources - Video

Gibbs Free Energy:

<https://www.youtube.com/watch?v=huKBuShAa1w&list=PLIIVwaZQkS2op2kDuFifhStNsS49LAXkZ&index=59>

Driving NonSpontaneous Reactions:

<https://www.youtube.com/watch?v=PFQM20ugoT8&list=PLIIVwaZQkS2op2kDuFifhStNsS49LAXkZ&index=60>